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Non-aggregating phthalocyanines with bulky 2,4-di-*tert*-butylphenoxy-substituents

M. Salih Ağırtaş*

Department of Chemistry, Faculty of Art and Science, Kafkas University, 36100 Kars, Turkey

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Abstract

In this paper, a bulky (2,4-di-*tert*-butylphenoxy)-substituted phthalonitrile was synthesized by nucleophilic displacement of nitro group in 4-nitro-phthalonitrile with 2,4-di-*tert*-butylphenol. Its cyclotetramerization in the presence of zinc(II), cobalt(II), nickel(II) or copper(II) ion with catalytic amount of DBU resulted in phthalocyanines being extensively soluble in number of organic solvents. Aggregation did not occur even in concentrations up to 1×10^{-3} M. The new compounds were characterized by elemental analyses, UV–vis, IR and NMR spectra.

Keywords: Phthalonitrile derivatives; Phthalocyanine; Nucleophilic displacement; Metal complexes; Aggregation

1. Introduction

Phthalocyanine (Pc) has been the subject of great deal of wide-ranging research for over 65 years. This has led to over 7000 citations of Pc in Chemical Abstracts, most of which are patents. The synthesis of a variety of substituted Pcs both metallo and non-metallo has been reported [1–3]. The main purpose for these substitutions has been to enhance Pc's very limited solubility [4–7]. Nowadays there is renewed interest in phthalocyanine chemistry, as phthalocyanines and many of their derivatives exhibit noteworthy properties for applications in materials science [1,8]. For example, phthalocyanines are used in laser-beam printer and photocopiers [9–13], in optical data storage, as liquid crystals, as photosensitizers, in non-linear optics, as gas sensors [14], as electrochromic substances [15], Langmuir–Blodgett films [16], and as carrier generation materials in near infrared (NIR) [1,7]. Many substituted derivatives of phthalocyanines behave like active components in various redox processes, for example, in photoredox reactions and photooxidations in solutions [17] and for photodynamic cancer therapy [18]. Aza analog of phthalocyanine are receiving considerable attention as photoinactivators in textile bleaching, in controlling growth of microorganisms, and as electrocatalysts in oxygen reduction. In addition, due to the ability of certain Pc derivatives to efficiently photoinactivate cancer cells in vivo [18] and viruses in stored blood, these have received particular attention. The design of Pc derivative with optimal pharmacokinetic and photodynamic properties largely depends on understanding the structure–activity relationships of this class of compounds.

Aggregation at relatively low concentrations, even in the range of 1×10^{-5} M, is frequently encountered in Pcs. In order to prevent aggregation, inclusion of large bulky groups on periphery has been proposed. In the present work, 2,4-di-*tert*-butylphenoxy-group has been preferred as the bulky group.

We now describe a synthetic route to a novel class of functional macrocycle with (2,4-di-*tert*-butylphenoxy)-substituents.

2. Experimental

Routine IR spectra were recorded on a Mattson 1000 FTIR spectrometer in KBr pellets, electronic spectra on a Shimadzu

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* Fax: +90 474 2122706.
E-mail address: salihagirtas@hotmail.com

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UV–vis spectrophotometer. ^1H NMR spectra were recorded on a Bruker 200 MHz spectrometer with tetramethylsilane as the internal standard. Elemental analyses results were found in good agreement with calculated values. 4-Nitrophthalonitrile was synthesized according to published procedures [19].

All other reagents and solvents were of reagent-grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego [20] and the solvents were stored over molecular sieves (4 Å).

*2.1. 4-(2,4-di-tert-butylphenoxy)phthalonitrile (**1**)*

4-Nitrophthalonitrile (1.73 g, 0.01 mol) was dissolved in *N*,*N*-dimethylformamide (30 cm^3) under nitrogen and 2,4-di-*tert*-butylphenol (2.06 g, 0.01 mol) was added. After stirring for 15 min, finely ground anhydrous potassium carbonate (5.2 g, 0.038 mol) was added in portions during 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature for 24 h. Then the mixture was poured into 100 ml water, and extracted with CH_2Cl_2. The crude product was washed first with 10% $NaHCO_3$ and then with water and dried over anhydrous sodium sulfate. The product was evaporated to dryness. The residue was recrystallized from ethanol. The yield was 2.5 g (78%). Mp: 150–151 °C. $C_{22}H_{24}N_2O$ (332.4 g/mol). IR (KBr) ν_{max} (cm^{-1}): 3075, 2995, 2958, 2868, 2230, 1594, 1484, 1397, 1312, 1277, 1248, 1088, 839. ^1H NMR ($CDCl_3$): $\delta = 7.73$ (1H, dd, 0.98 and 8.4 Hz, Ar–H), 7.49 (1H, d, 2.4 Hz, Ar–H), 7.27 (3H, m, Ar–H), 6.76 (1H, d, 8.4 Hz, Ar–H), 1.35 (9H, s, $C(CH_3)_3$) and 1.33 (9H, s, $C(CH_3)_3$). ^{13}C NMR (DMSO): $\delta = 29.9$, 31.1, 34.3, 34.4, 107.5, 115.3, 115.8, 116.6, 120.9, 121.5, 122.5, 124.2, 124.7, 136.2, 140.0, 147.6, 149.9, 161.2.

*2.2. Tetrakis[(2,4-di-tert-butylphenoxy)-phthalocyaninato]zinc (**2**)*

4-(2,4-Di-*tert*-butylphenoxy)phthalonitrile (0.166 g, 0.0005 mol) and metal salt ($ZnCl_2$, 0.017 g) were dissolved in *N*,*N*-dimethylformamide (0.8 cm^3) under nitrogen and in the presence of DBU (0.05 ml). Then the mixture was heated and stirred at 155 °C for 8 h under N_2 atmosphere. After that it was cooled to room temperature; the reaction mixture was precipitated by adding it drop wise into ethanol (20 ml). The crude product was purified by column chromatography (silica, $CHCl_3$). This phthalocyanine is soluble in chloroform, dichloromethane, THF, toluene, DMF and DMSO. The yield was 0.125 g (85.6%); Calcd. for $C_{72}H_{64}N_8O_4Zn$: C, 73.95; H, 5.47; N, 9.58%. Found: C, 74.03; H, 5.26; N, 9.63%; IR (KBr) ν_{max} (cm^{-1}): 3071, 2960, 2912, 2862, 1594, 1486, 1313, 1277, 1249, 1088, 840; UV–vis (DMF) λ_{max} ($\log \varepsilon$) (nm): 358 (3.68), 612 (3.40), 680 (4.09).

*2.3. Tetrakis[(2,4-di-tert-butylphenoxy)-phthalocyaninato]cobalt (**3**)*

4-(2,4-Di-*tert*-butylphenoxy)phthalonitrile (0.166 g, 0.0005 mol) and metal salt ($CoCl_2$, 0.017 g) were dissolved in *N*,*N*-dimethylformamide (1 cm^3) under nitrogen and in the presence of DBU. Then the mixture was refluxed for 9 h under N_2 atmosphere. After that it was cooled to room temperature, the tube was opened and a dark green product was obtained. The crude product was washed several times with EtOH to dissolve any unreacted metal salt. For further purification $CHCl_3$ was added in order to dissolve the crude product, which was then filtered off and dried. The product is soluble in chloroform, dichloromethane, THF, toluene, DMF and DMSO. The yield was 0.020 g (13.8%); Calcd. for $C_{72}H_{64}N_8O_4Co$: C, 74.40; H, 5.50; N, 9.63%. Found: C, 74.02; H, 5.60; N, 9.52%; IR (KBr) ν_{max} (cm^{-1}): 3072, 2959, 2868, 1615, 1472, 1262, 1233, 1091; UV–vis ($CHCl_3$) λ_{max} ($\log \varepsilon$) (nm): 609 (3.57), 675 (4.17).

*2.4. Tetrakis[(2,4-di-tert-butylphenoxy)-phthalocyaninato]nickel (**4**)*

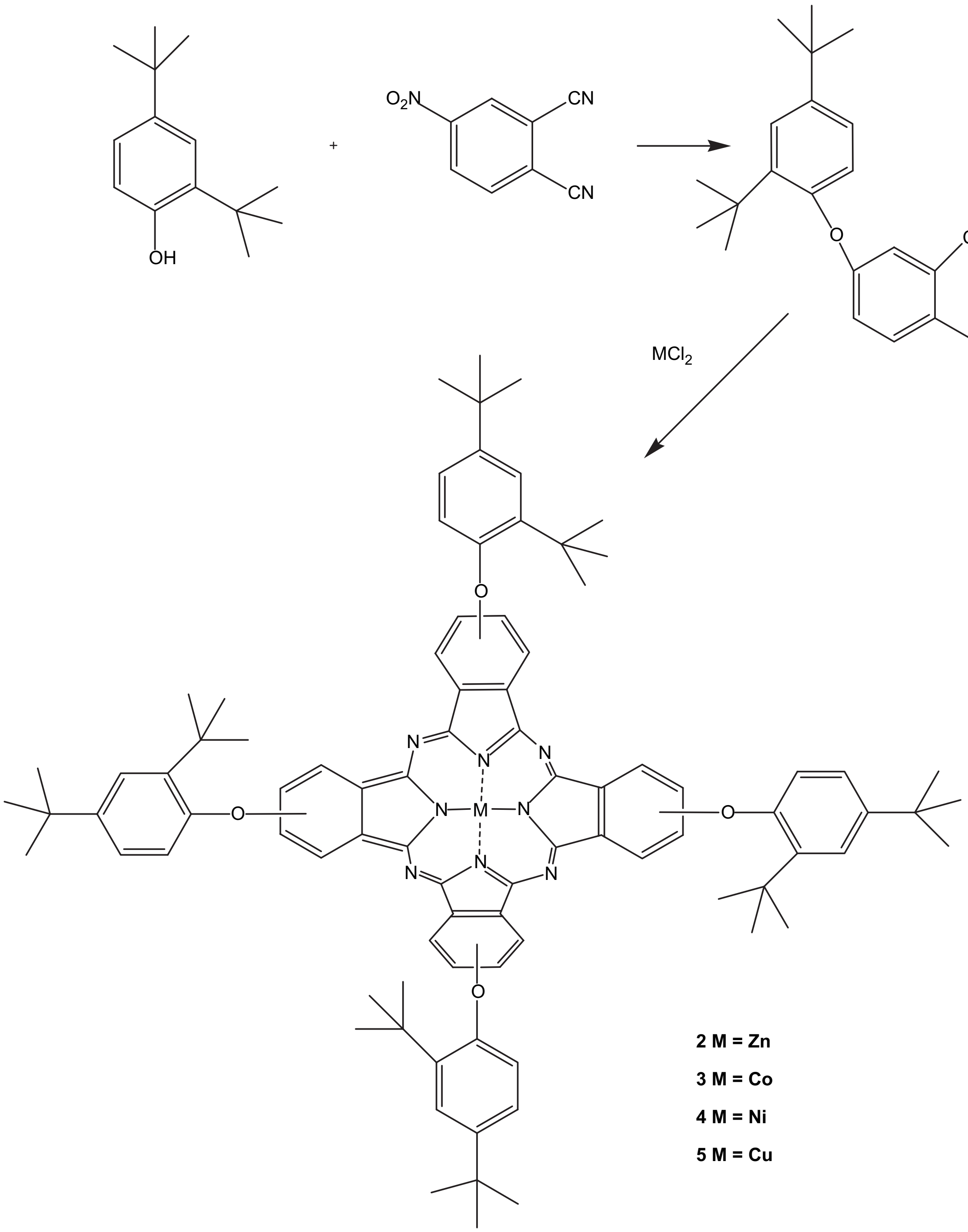
4-(2,4-Di-*tert*-butylphenoxy)phthalonitrile (0.100 g, 0.0003 mol) and metal salt ($NiCl_2$, 0.0098 g) were dissolved in *N*,*N*-dimethylformamide (0.8 cm^3) under nitrogen and in the presence of DBU. Then the mixture was refluxed for 9 h under N_2 atmosphere. After that it was cooled to room temperature, the tube was opened and a dark green product was obtained. The crude product was washed several times with EtOH to dissolve any unreacted metal salt. For further purification $CHCl_3$ was added in order to dissolve the crude product, which was then filtered off and dried. The product is soluble in chloroform, dichloromethane, THF, toluene, DMF and DMSO. The yield was 0.019 g (21.8%); Calcd. for $C_{72}H_{64}N_8O_4Ni$: C, 74.38; H, 5.50; N, 9.63%. Found: C, 74.07; H, 5.11; N, 9.51%; IR (KBr) ν_{max} (cm^{-1}): 3073, 2958, 2923, 2862, 1616, 1481, 1472, 1264, 1235, 1091; UV–vis ($CHCl_3$) λ_{max} ($\log \varepsilon$) (nm): 609 (3.75), 677 (4.28).

*2.5. Tetrakis[(2,4-di-tert-butylphenoxy)-phthalocyaninato]copper (**5**)*

4-(2,4-Di-*tert*-butylphenoxy)phthalonitrile (0.100 g, 0.0003 mol) and metal salt ($CuCl_2$, 0.010 g) were dissolved in ethanol (1.5 cm^3) under nitrogen and in the presence of DBU. Then the mixture was refluxed for 24 h under N_2 atmosphere. After that it was cooled to room temperature and the tube was opened. The crude product was washed several times with EtOH to dissolve any unreacted metal salt. For further purification $CHCl_3$ was added in order to dissolve the crude product, which was then filtered off and dried. The product is soluble in chloroform, dichloromethane, THF, toluene, DMF and DMSO. The yield was 0.020 g (22.8%); Calcd. for $C_{72}H_{64}N_8O_4Cu$: C, 74.07; H, 5.48; N, 9.59%. Found: C, 73.90; H, 5.20; N, 9.61%; IR (KBr) ν_{max} (cm^{-1}): 3071, 2959, 2868, 1614, 1470, 1398, 1267, 1232, 1088; UV–vis ($CHCl_3$) λ_{max} ($\log \varepsilon$) (nm): 339 (3.89), 616 (3.59), 685 (4.21).

3. Results and discussion

The synthetic route followed in this work is shown in Scheme 1. 4-(2,4-Di-*tert*-butylphenoxy)phthalonitrile



Scheme 1.

was prepared by nucleophilic displacement of nitro group in 4-nitro-phthalonitrile with 2,4-di-*tert*-butylphenol. Cyclotetramerization of the phthalonitrile derivative in the presence of metal salts (MCI_2) gave the desired metallophthalocyanines **2**–**5**.

The spectroscopic characterization of the newly synthesized compounds included elemental analyses, ^1H NMR, IR and UV–vis spectral investigations and the results are in accord with the proposed structures. In the IR spectrum of **1**,

Table 1
Electronic spectra of the phthalocyanines

Compound	λ_{max}/nm (10^{-4} ε/dm^3 mol^{-1} cm^{-1})
2[a]	680 (4.09), 612 (3.40), 358 (3.68)
3[b]	675 (4.17), 609 (3.57)
4[b]	677 (4.28), 609 (3.73)
5[b]	685 (4.21), 616 (3.59), 339 (3.89)

[a] In DMF.

[b] In $CHCI_3$.

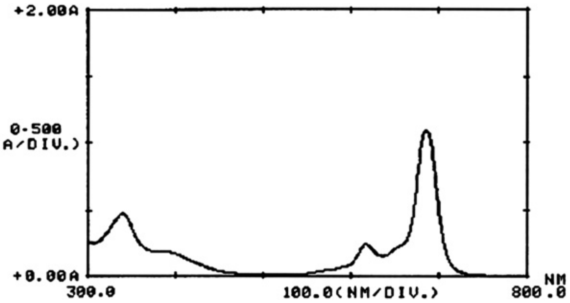


Fig. 1. Electronic spectra of **5** in chloroform (10^{-5} M).

the intense absorption band at 2230 cm^{-1}, corresponding to C≡N vibrations, disappears after its conversion into phthalocyanines (**2**, **3**, **4**, and **5**) [5–15]. The ^{1}H NMR spectrum of **1** indicates aromatic protons at $\delta = 7.73$, 7.49, 7.27, 6.76 and at 1.35–1.33 the aliphatic $C(CH_3)_3$ groups. The ^{1}H NMR spectrum of **2** is similar to that of **1**.

The UV–vis spectra of **3**–**5** recorded in chloroform and **2** in DMF show the typical pattern of phthalocyaninatometal complexes. They are dominated by the π–π* transitions within the heteroaromatic 18-π-electron system [7]. The electronic absorption spectra of the phthalocyanines **2**–**5** exhibited characteristic Q- and B-bands one in the visible region at 600–685 nm (Q-band) attributed to the π–π* transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the Pc^{2-} ring, and the other in the UV region at 300–400 nm, (B-band) arising from the deeper π-levels → LUMO transition [1,2] (Table 1).

Tetra(2,4-bis(*tert*-butyl)phenoxy substituted Pcs showed enhanced solubility in a number of organic solvents, e.g. chloroform, dichloromethane, THF, toluene, DMF and DMSO, etc. as expected. Another important feature of these compounds is the lower tendency to form aggregates [21–25]. In contrast to some soluble Pcs with long alkyl, alkyloxy, alkylthio substituents and even those with condensed crown ether groups on the periphery, the Pcs reported in this work showed hardly any aggregation up to a concentration range of 10^{-3} M (Figs. 1–3). This fact has been verified by the UV–vis investigations on solutions in the concentration range of 1×10^{-3}–1×10^{-5} M. The graph of molar absorptivity versus concentration gave a constant value in this concentration range.

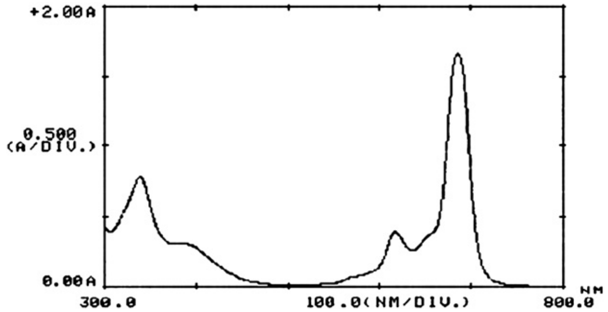


Fig. 2. Electronic spectra of **5** in chloroform (10^{-4} M).

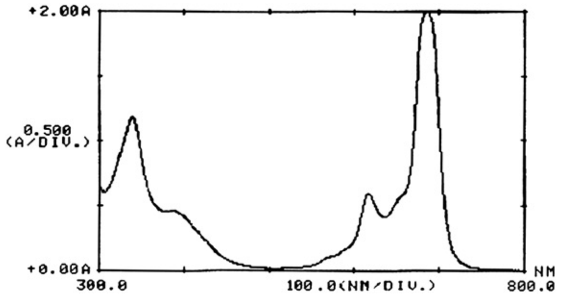


Fig. 3. Electronic spectra of **5** in chloroform (10^{-3} M).

The optical properties of Pcs are closely related to the presence of these compounds in solutions as monomeric units or oligomeric aggregates. Here in this work we have shown that the bulky 2,4-di-*tert*-butoxyphenyl groups can be efficient substituents to keep Pc macrocycles in monomeric state.

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